

Hydrogen productions using supercritical water - an update of progress at General Atomics

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General Atomics (GA) is actively developing Supercritical Water Gasification (SCWG) and Supercritical Water Partial Oxidation (SWPO) for the efficient conversion of low-grade biomass feedstocks (such as sewage sludge, municipal solid waste, and animal waste) to clean fuels, notably hydrogen, for power production and other end uses. Superior environmental performance results from the use of these various Supercritical Water (SCW) processes - with negligible emissions of criteria pollutants, including particulates, NO_x, SO_x, and hazardous air pollutants.

GA was recently selected by DOE's Hydrogen Program to perform cooperatively-funded research on SWPO of composted sewage sludge and municipal solid waste (MSW) to generate hydrogen. This research will be performed in GA's privately funded SCW pilot plant at GA's facilities in San Diego, CA. This pilot plant is a logical next step beyond the sewage sludge SCWG test program conducted by GA for the DOE Hydrogen Program in 1997, and the SCWG test program to gasify slurries containing 40 wt% composted sewage sludge and MSW conducted in 1999 by GA and Environmental Energy Systems, Inc. (EESI) for the California Energy Commission's Public Interest Energy Research (PIER) Program.

SWPO involves carrying out oxidative reactions in the SCW environment – akin to high-pressure steam – in the presence of sub-stoichiometric quantities of an oxidant, typically pure oxygen. The key advantage of the SWPO process is the use of partial oxidation in-situ to rapidly heat the gasification medium, resulting in less char formation and improved hydrogen yields. Another major advantage is the high-pressure, high-density aqueous environment that is ideal for reacting and gasifying organics. The high density also allows utilization of compact equipment that minimizes capital cost and footprint requirements.

In SCWO, heavy slurries of organic fuels such as biomass are pressurized to above the critical point of water (typically 3400 psia), combined with oxygen from a liquid oxygen source and heated to reaction temperature. SCWO oxidation reactions occur rapidly to further heat the medium to full operating temperatures of about 1200° to 1650°F. In SCWG, similar characteristics are required, except without oxygen. Heating is accomplished through a heat exchange surface to bring the slurry to gasification conditions and the production of synthesis gas rich in hydrogen. In SWPO, partial oxidation is used for rapidly heating the slurry through the transition temperature to improve the yield of hydrogen and reduce char.

GA has already carried out substantial development on these SCW core technologies. GA has developed advanced down-flow SCWO reactors featuring corrosion-resistant removable liners that enable high-temperature reaction zones and low-temperature pressure vessels, thus enabling larger sizes and lower cost pressure vessels. GA has developed heavy slurry mixing and high-pressure pumping systems, high-pressure pre-heaters, and high-pressure heat recovery heat exchangers that apply to SCW processes. Hydroclones have been developed to remove particulates from the SCW effluents. Additionally, packed bed ceramic filters have been evaluated for hot filtration of SCW effluent. Applications of SCWO technology have thus far been primarily targeted at waste destruction applications, where the high destruction efficiencies attainable in compact equipment are very desirable. The process has the capability of operating on a wide range of feed materials, including chemical agents, explosives, and wet wastes such as sewage sludge.

SCWG is an emerging technology focused at production of synthesis gas from low-grade feedstocks. Complete gasification has been reported in the laboratory for some biomass feedstocks. A complete absence of char has also been reported in most cases. As with SCWO, rapid reaction times and a relatively dense medium make for compact, heat-efficient equipment in the SCWG process. Following purification, the SCWG gaseous effluent product may be supplied to fuel cells for high-efficiency electricity production.

SWPO combines elements of both fully oxidizing SCWO (heat generation via oxidation) and fully reducing SCWG (gas production via heat absorption). The rapid heating accomplished by in-situ partial oxidation is expected to further reduce char formation and increase hydrogen yields.

The gas and liquid emissions from SCWO oxidation processes are very clean and readily discharged. NO_x and SO_x are extremely low, typically less than 1 ppm, while CO is typically between 1 to 10 ppm. The gas leaves the process at a low temperature and with low-moisture content, so a smoke or steam plume is not present. Liquid effluent typically contains less than 1 ppm of organic carbon and is near-drinking-water quality. Solid effluents from SCWO and SCWG processes have been shown to pass the TCLP requirements for disposal. An additional benefit of the SCW processes is that the high pressure facilitates CO_2 sequestration. By combining pressure with the cold sink available from the liquid oxygen oxidant, CO_2 can be readily liquefied. It may then be recycled, injected for oil recovery, or otherwise handled to reduce greenhouse emissions.

SCW processes are based on the unique properties of water at conditions near and beyond its thermodynamic critical point of 705°F and 3206 psia. At typical SCW reactor conditions of 1200°F and 3400 psi, densities are only one-tenth that of normal liquid water. Hydrogen bonding is almost entirely disrupted, so that the water molecules lose the ordering responsible for many of liquid water's characteristic properties. In particular, solubility behavior is closer to that of high-pressure steam than to liquid water. The loss of bulk polarity by the water phase has striking effects on normally water-soluble salts. No longer readily solvated by water molecules, they frequently precipitate out as solids.

Small polar and nonpolar organic compounds, with relatively high volatility, will exist as vapors at typical SCW conditions, and hence will be completely miscible with supercritical water. Gases such as N_2 , O_2 , and CO_2 show similar complete miscibility. Larger organic compounds and polymers will hydrolyze to smaller molecules at typical SCW conditions, thus resulting in solubilization via chemical reaction. The molecular dispersion of the organic and oxidant reactants within a single phase, in conjunction with the high diffusivity, low viscosity, and relatively dense SCW reaction medium, is conducive to rapid reactions. Furthermore, the temperature is sufficiently high that reaction completion is usually attained within seconds to tens of seconds. Rapid reaction rates have been demonstrated for virtually all types of organic materials, including solids.

SCW processes continue to show promise as advanced methods for the conversion of biomass and low-grade fuels to energy products such as synthesis gas rich in hydrogen, process heat, and eventually electricity. SCWO systems are currently being commercialized by GA for difficult waste destruction applications that are required to have very low emissions. This commercialization experience will be important to continuing development efforts for producing hydrogen from biomass feedstocks.

GA's accomplishments and progress are presented for current pilot plant development and testing of SWPO, and ongoing evaluations of the commercial prospects of biomass processing, hydrogen production and power generation.